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54 **Process for producing branched alpha-olefin polymers.**

57 A process for homopolymerizing an  $\alpha$ -olefin branched at the carbon atom of the third position or copolymerizing said  $\alpha$ -olefin with another olefin in the presence of a catalyst system comprising a combination of an organo-aluminum compound and a solid catalyst component containing titanium, chlorine and a hydrocarbyloxy group, of which the X-ray diffraction spectrum has the diffraction lines at least corresponding to the diffraction lines of planes [113] and [300] of titanium trichloride having a layer structure and wherein the content of the hydrocarbyloxy group is 0.01 to 0.3 mole per 1 mole of titanium.

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PROCESS FOR PRODUCING BRANCHED  $\alpha$ -OLEFIN POLYMERS

1           The present invention relates to a process for  
producing a branched  $\alpha$ -olefin polymer. It is known  
that the melting point of <sup>an</sup>isotactic polymer of <sup>a</sup>branched  
 $\alpha$ -olefin generally tends to increase when the degree of  
5   branching increases and when the position of the branching  
approaches the position of carbon-carbon double bond.  
Accordingly, isotactic polymers of branched  $\alpha$ -olefins and  
particularly those having the branch at the carbon atom of  
the third position are excellent in heat resistance and  
10   useful as industrial material.

Like usual  $\alpha$ -olefins, branched  $\alpha$ -olefins can  
also be polymerized with Ziegler catalysts. Unlike  $\alpha$ -  
olefins, however, in case of branched  $\alpha$ -olefins, the  
polymerization activity lowers extremely as compared with  
15   that of  $\alpha$ -olefins, and such low       polymerizing  
activity is particularly remarkable when the branch is  
located on the carbon atom of the third position.

Various processes for polymerizing branched  
 $\alpha$ -olefins were       proposed in, for example, Japanese  
20   Patent Application Kokai (Laid-Open) Nos. 59,989/76,  
195,704/82, 182,305/82 and 8,708/83. However, when  
branched  $\alpha$ -olefins are polymerized by these processes, the  
polymerization activity is still not sufficiently high.

The present inventors conducted elaborated studies  
25   with the aim of finding a catalyst system showing a high

1 activity on the polymerization of branched  $\alpha$ -olefins.

As the result, it was found that a catalyst system comprising a combination of an organo-aluminum compound and a solid catalyst component containing titanium,

5 chlorine and hydrocarbyloxy group shows a polymerization activity several times higher than that exhibited by the catalyst systems used in the above-mentioned known processes. Based on this finding, the present invention has been accomplished.

10 It is an object of this invention to provide a novel solid catalyst component for polymerizing branched  $\alpha$ -olefins.

It is another object of this invention to provide a process for polymerizing branched  $\alpha$ -olefins by using  
15 the novel solid catalyst component.

Other objects and advantages of this invention will become apparent from the descriptions presented below.

According to this invention, there is provided a process for homopolymerizing an  $\alpha$ -olefin branched at  
20 the carbon atom of the third position or copolymerizing said  $\alpha$ -olefin with another olefin in the presence of a catalyst system comprising a combination of an organo-aluminum compound and a solid catalyst component containing titanium, chlorine and <sup>a</sup>hydrocarbyloxy group, of which the  
25 X-ray diffraction spectrum has the diffraction lines at least corresponding to the diffraction lines of planes [113] and [300] of titanium trichloride having a layer structure and of which <sup>the</sup>hydrocarbyloxy group content is

1 0.01 to 0.3 mole per 1 mole of titanium.

This invention is characterized in that, when an  $\alpha$ -olefin branched at the carbon atom of the third position is polymerized by using the catalyst system of this invention, a polymerization activity of several times higher than that achievable in the known processes can be obtained.

The solid catalyst component containing titanium, chlorine and/<sup>a</sup>hydrocarbyloxy group, provided by this invention gives an X-ray diffraction spectrum having diffraction lines at least corresponding to the diffraction lines of planes [113] and [300] of titanium trichloride having a layer structure, and contains 0.01 to 0.3 mole of/<sup>a</sup>hydrocarbyloxy group per 1 mole of titanium.

15 The hydrocarbyloxy group is represented by the general formula  $OR^1$ , wherein  $R^1$  represents a hydrocarbon group having 1 to 20 carbon atoms. Concrete examples of  $R^1$  include alkyl groups, such as methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, n-amyl, iso-amyl, n-hexyl, 20 n-heptyl, n-octyl, n-decyl, n-dodecyl and the like; aryl groups, such as phenyl, cresyl, xylyl, naphthyl and the like; cycloalkyl groups, such as cyclohexyl, cyclopentyl and the like; allyl groups, such as propenyl and the like; and aralkyl groups, such as benzyl and the like. Among them, 25 straight chain alkyl groups having 2 to 18 carbon atoms and aryl groups having 6 to 18 carbon atoms are particularly preferred. Said hydrocarbyloxy group may also be two or more kinds of different hydrocarbyloxy groups. The

1 content of the hydrocarbyloxy group in the solid catalyst  
component is 0.01 to 0.3 mole and preferably 0.02 to 0.25  
mole, per 1 mole of titanium.

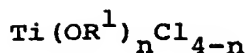
Further, the X-ray diffraction spectrum of  
5 said solid catalyst component must have the diffraction  
lines at least corresponding to the diffraction  
lines of planes [113] and [300] of titanium trichloride  
having a layer structure. As used herein, the term "titanium  
trichloride having a layer structure" means the titanium  
10 trichlorides mentioned in G. Natta et al.: J. Polymer  
Sci., 51, 399 (1961), wherein the examples include <sup>the</sup>  $\alpha$ -,  $\gamma$ -  
and  $\delta$ -form titanium trichlorides. The X-ray diffraction  
spectrum of the solid catalyst component of this inven-  
tion shows its diffraction lines at least at the lattice  
15 spacing (d) of 2.72 - 2.52 Å and 1.78 - 1.76 Å. Preferably,  
the solid catalyst component of this invention gives an  
X-ray diffraction spectrum having diffraction lines at  
least corresponding to the diffraction lines of planes  
[113] and [300] of the  $\delta$ -form titanium trichloride (d =  
20 2.71 Å and 1.77 Å).

As examples of the synthetic procedure of such  
a solid catalyst component, the following methods can be  
illustrated.

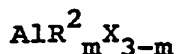
#### Synthetic Method (I)

25 This is a method which comprises reducing a  
titanium compound represented by the following general  
formula:

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- 1 wherein  $\text{R}^1$  represents hydrocarbon group having 1 - 20 carbon atoms and  $n$  represents a numerical figure satisfying  $0 < n \leq 4$ , with an organo-aluminum compound represented by the following general formula:



- 5 wherein  $\text{R}^2$  represents<sup>a</sup> hydrocarbon group having 1 - 20 carbon atoms,  $\text{X}$  represents<sup>a</sup> halogen atom and  $m$  represents a numerical figure satisfying  $1 < m \leq 3$ , to obtain a hydrocarbyloxy group-containing solid product insoluble in hydrocarbon solvents, followed by treating said solid product with an ether compound and titanium tetrachloride in the state of a slurry at a temperature of 45°C to 120°C.

- 10 In/<sup>the</sup>Synthetic Method (1),  $\text{R}^1$  in the titanium compound represented by the general formula  $\text{Ti}(\text{OR}^1)_n\text{Cl}_{4-n}$  is a hydrocarbon group having 1 - 20 carbon atoms, and preferably a straight chain alkyl group having 2 - 18 carbon atoms or an aryl group having 6 - 18 carbon atoms.

A good result can be obtained when  $n$  satisfies  $0 < n \leq 4$  and particularly when  $n$  satisfies  $1 \leq n \leq 4$ .

- 20 Concrete examples of the organo-aluminum compound represented by/<sup>the</sup>general formula  $\text{AlR}^2_m\text{X}_{3-m}$  ( $\text{R}^2$  represents<sup>a</sup> hydrocarbon group having 1 - 20 carbon atoms,  $\text{X}$  represents<sup>a</sup> halogen atom, and  $m$  represents a numerical figure satisfying  $1 < m \leq 3$ ), used in the reduction, include

1 ethylaluminum sesquichloride, dimethylaluminum chloride,  
diethylaluminum chloride, di-n-propylaluminum chloride,  
trimethylaluminum, triethylaluminum, tri-isobutylaluminum,  
ethylidicyclohexylaluminum, triphenylaluminum, diethyl-  
5 aluminum hydride, di-isobutylaluminum hydride, diethyl-  
aluminum bromide, diethylaluminum iodide and the like.

Among them, diethylaluminum chloride and  
ethylaluminum sesquichloride give particularly good  
results.

10 The reduction is carried out preferably after  
diluting the titanium compound and the organo-aluminum  
compound to a concentration of 10 - 70% by weight with an  
inert hydrocarbon solvent, such as pentane, hexane, heptane,  
octane, decane, toluene or decalin.

15 The reaction temperature of the reduction is  
-10°C to 80°C, and preferably 0°C to 70°C. Although <sup>the</sup> time  
of the reduction is not critical, it is preferably 1 to  
6 hours.

The molar ratio of the titanium compound to the  
20 organo-aluminum compound can arbitrarily be varied  
depending on the purpose. A good result can be obtained  
by using 0.5 to 1.5 moles of diethylaluminum chloride or  
1.5 to 2.5 moles of ethylaluminum sesquichloride per 1 mole  
of the titanium compound. It is also allowable to carry  
25 out after reaction at 30° to 100°C after completion of the  
reduction.

The hydrocarbyloxy group-containing solid product  
insoluble in hydrocarbon solvents, obtained by the reduction,

1 is separated from the liquid phase, washed several times  
with an inert hydrocarbon solvent, such as pentane, hexane,  
heptane, octane, decane, toluene, xylene, decalin or the  
like, and then reacted with an ether compound and titanium  
5 tetrachloride. As said ether compound, dialkyl ethers,  
such as diethyl ether, di-n-propyl ether, di-isopropyl  
ether, di-n-butyl ether, di-n-amyl ether, di-isoamyl ether,  
di-neopentyl ether, di-n-hexyl ether, di-n-octyl ether,  
methyl n-butyl ether, methyl isoamyl ether, ethyl isobutyl  
10 ether and the like are preferable, among which di-n-butyl  
ether and di-isoamyl ether are particularly preferred.  
Said ether compound is used in an amount of 0.1 to 5 moles  
and preferably 0.3 to 3 moles per 1 mole of the titanium  
atom contained in the hydrocarbyloxy group-containing  
15 solid product. The titanium tetrachloride is added in  
an amount of 0.1 to 10 moles and preferably 0.5 to 5 moles  
per 1 mole of the titanium atom contained in the solid  
product. The ratio of the titanium tetrachloride to the  
ether compound is 0.5 mole to 10 moles and preferably  
20 1.5 moles to 5 moles per 1 mole of the ether compound.

The reaction among the hydrocarbyloxy group-  
containing solid product insoluble in hydrocarbon solvents  
and the ether compound and titanium tetrachloride is  
carried out in the state of a slurry. As the solvent used  
25 for making a slurry from the hydrocarbyloxy group-containing  
solid product, aliphatic hydrocarbons, such as pentane,  
hexane, heptane, octane, decane and the like, aromatic  
hydrocarbons, such as toluene, xylene, decalin and the like



1 and alicyclic hydrocarbons, such as cyclohexane, methyl-  
cyclohexane and the like can be referred to. The con-  
centration of the slurry is 0.05 to 0.5 g-solid/ml-solvent,  
and preferably 0.1 to 0.3 g-solid/ml-solvent. The reaction  
5 temperature is 45° to 120°C and preferably 60° to 100°C.  
Although the time of the reaction is not critical, it is  
usually 30 minutes to 6 hours.

Addition of the solid product, the ether compound  
and the titanium tetrachloride may be carried out by any  
10 of the methods of adding the ether compound and titanium  
tetrachloride to the solid product and the inverse method  
of adding the solid product into a solution of the ether  
compound and titanium tetrachloride. In the method of adding  
the ether compound and titanium tetrachloride to the solid  
15 product, the procedure of addition may be any of the  
successive addition (addition of ether compound followed  
by addition of titanium tetrachloride) and the simultaneous  
addition of them.

The solid catalyst component obtained by the  
20 above-mentioned reaction is separated from the liquid phase,  
washed several times with an inert hydrocarbon solvent,  
such as hexane, heptane or the like, and then used for  
polymerization.

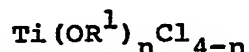
#### Synthetic Method (II)

25 This is a method which comprises reducing titanium  
tetrachloride with an organo-aluminum compound represented  
by the general formula  $AlR_m^2X_{3-m}$  ( $R^2$ , X and m are each as

1 defined previously), heat-treating the reduced product  
at a temperature not higher than 150°C to obtain a heat-  
treated solid product, reacting the heat-treated solid  
product in a hydrocarbon solvent with a mixture comprising  
5 a halogen compound represented by the following general  
formula:



(X represents a halogen atom) and an ether compound, and  
treating the reaction product with a titanium compound  
represented by the following general formula:



10 ( $R^1$  and n are each as defined previously).

The organo-aluminum compound represented by the  
general formula  $AlR^2_mX_{3-m}$  ( $R^2$ , X and m are each as defined  
previously) used in the reduction of this synthetic method  
is the same as that used in <sup>the</sup> Synthetic Method (I). Par-  
15 ticularly, ethylaluminum sesquichloride and diethylaluminum  
chloride give good results.

The reduction is preferably carried out in an  
inert hydrocarbon solvent, particularly aliphatic hydro-  
carbon solvents such as hexane, heptane and the like,  
20 at a temperature of -50°C to 50°C, particularly -30°C  
to 30°C. Concretely saying, it is preferable to add a  
solution of the organoaluminum compound in an inert

- 1 hydrocarbon to a solution of titanium tetrachloride in  
an inert hydrocarbon so slowly as to maintain the system  
at the predetermined temperature. The concentrations of  
titanium tetrachloride and the organo-aluminum compound  
5 in the inert hydrocarbon solution are both in the range of from  
20 to 80% by weight and preferably in the range of <sup>from</sup> 30 to  
60% by weight. The ratio of <sup>the</sup> organo-aluminum compound  
represented by the general formula  $AlR_m^2X_{3-m}$  to titanium  
tetrachloride used in the reaction is  $m^{-1}$  to  $2 \times (m-1)^{-1}$  mole  
10 organo-aluminum compound and preferably  $1 \times (m-1)^{-1}$  to  
 $1.5 \times (m-1)^{-1}$  mole organo-aluminum compound, per 1 mole of  
titanium tetrachloride. (Here, the molar number of organo-  
aluminum compound is counted as a monomer.) Preferably,  
the reduction is carried out with an appropriate stirring.  
15 After mixing titanium tetrachloride with the organo-aluminum  
compound, the system is preferably stirred at a temperature  
falling in the above-mentioned reaction temperature range  
for 15 minutes to 6 hours to complete the reduction. Thus,  
a suspension of the reduced solid product is obtained.  
20 The heat-treatment may be performed after  
separating the reduced solid product from the suspension  
formed by the reduction and then washing it with an inert  
hydrocarbon solvent. More preferably, however, the heat-  
treatment is carried out by directly using the suspension  
25 of reduced solid product as it is. The heat-treatment can  
be performed by heating the suspension of reduced solid  
product at a temperature not higher than 150°C, preferably  
at a temperature of 50° to 120°C. The optimum temperature

1 of the heat treatment varies depending on the kind of  
organo-aluminum compound used in the reduction. For example,  
the optimum temperature of heat treatment is 50° to 100°C  
when the organo-aluminum compound is ethylaluminum  
5 sesquichloride, and it is 75° to 110°C when the organo-  
aluminum compound is diethylaluminum chloride. The time of  
the heat treatment is usually <sup>of</sup> 15 minutes to 6 hours, and  
preferably <sup>of</sup> 30 minutes to 4 hours. After the heat treatment,  
the solid product is separated from the liquid phase and  
10 washed with an inert hydrocarbon solvent to obtain a heat-  
treated solid product.

The halogen compound is represented by the general  
formula  $X_2$ , wherein X represents Cl, Br or I. Preferably,  
X is I. The halogen compound is used in an amount of  $10^{-5}$   
15 mole to  $5 \times 10^{-2}$  mole and preferably  $10^{-4}$  mole to  $10^{-2}$  mole,  
per 1 g of the heat-treated solid product.

Preferably, the halogen compound is used in the  
form of a solution in a hydrocarbon solvent and/or an ether  
compound.

20 As said ether compound, the same one as in the  
Synthetic Method (I) is used. Particularly preferred  
ether compounds are di-n-butyl ether and di-isoamyl ether.  
The ether compound is used in an amount of  $10^{-4}$  mole to  
0.03 mole, preferably  $10^{-3}$  mole to 0.02 mole, and par-  
25 ticularly preferably 0.002 mole to 0.01 mole, per 1 g of  
the heat-treated solid product.

The reaction between the heat-treated solid  
product and a mixture composed of the halogen compound

1 and the ether compound is carried out in a hydrocarbon  
solvent. Concrete examples of said hydrocarbon solvent  
include aliphatic hydrocarbons, such as hexane, heptane,  
octane, decane and the like and aromatic hydrocarbons such  
5 as benzene, toluene, xylene and the like. The concentration  
of the heat-treated solid product in the hydrocarbon  
solvent is 50 to 500 g/liter and preferably 100 to 400 g/  
liter. The reaction temperature is 50° to 120°C and  
preferably 70° to 100°C. Preferably, the reaction is  
10 carried out while stirring a suspension of <sup>the</sup> heat-treated  
solid product. The time of the reaction is preferably in  
the range of <sup>from</sup> 5 minutes to 6 hours, and particularly in  
<sup>from</sup> the range of 15 minutes to 2 hours.

After the reaction, the solid product is separated  
15 from the liquid phase, washed with an inert hydrocarbon  
solvent and then treated with a titanium compound represented  
by the general formula  $Ti(OR^1)_nCl_{4-n}$ . Alternatively,  
without separating the solid product from the liquid phase  
the titanium compound represented by the general formula  
20  $Ti(OR^1)_nCl_{4-n}$  is directly added to the reacted suspension  
and then a heat treatment is carried out. In the titanium  
compound represented by the above-mentioned general formula  
 $Ti(OR^1)_nCl_{4-n}$  wherein  $R^1$  represents <sup>a</sup> hydrocarbon group  
having 1 to 20 carbon atoms and n represents a numerical  
25 figure satisfying  $0 < n \leq 4$ ,  $R^1$  is preferably a straight  
chain alkyl group having 2 to 18 carbon atoms or an aryl  
group having 6 to 18 carbon atoms. The numerical figure  
n must satisfy  $0 < n \leq 4$  and preferably  $0.2 \leq n \leq 2$ .

1 The treatment with the titanium compound represented by  
the general formula  $Ti(OR^1)_nCl_{4-n}$  is carried out in a  
hydrocarbon solvent. The concentration of  $Ti(OR^1)_nCl_{4-n}$   
is not lower than 5% by volume, and preferably 15 to 60%  
5 by volume. The temperature of the treatment is 0° to  
100°C, and preferably 40° to 80°C. The time of the treat-  
ment is 5 minutes to 4 hours, and preferably 15 minutes  
to 2 hours. The solid catalyst component obtained by the  
above-mentioned reaction is separated from the liquid phase,  
10 washed several times with an inert hydrocarbon solvent,  
such as hexane, heptane or the like, and then used for  
polymerization.

Next, as the organo-aluminum compounds usable  
for the polymerization of olefins in this invention,  
15 trialkylaluminums, dialkylaluminum hydrides, dialkyl-  
aluminum chlorides, dialkylaluminum alkoxides, dialkyl-  
aluminum siloxides and their mixtures can be referred to.  
Examples of the preferably usable organo-aluminum compound  
include dimethylaluminum chloride, diethylaluminum  
20 chloride, di-isobutylaluminum chloride, diethylaluminum  
bromide, diethylaluminum iodide, trimethylaluminum,  
triethylaluminum, tri-isobutylaluminum, diethylaluminum  
hydride, diethylaluminum ethoxide and mixtures thereof.  
Among them, trimethylaluminum, triethylaluminum, tri-  
25 isobutylaluminum, diethylaluminum ethoxide and mixtures  
thereof are particularly preferred. The organo-aluminum  
compound is used in an amount of 0.5 mole to 100 moles  
and preferably 1 mole to 50 moles, per 1 mole of titanium

1 atom present in the solid catalyst component.

The branched  $\alpha$ -olefins used in this invention are  $\alpha$ -olefins branched at the carbon atom of the third position. Concrete examples of such branched  $\alpha$ -olefin  
5 include 3-methylbutene-1, 3-methylpentene-1, 3-ethylpentene-1, 3-methylhexene-1, 3,5-dimethylhexene-1, vinylcyclopentane, vinylcyclohexane, 4-vinylcyclohexene-1 and the like. Among these branched  $\alpha$ -olefins, 3-methylbutene-1 and vinylcyclohexane are particularly preferred. The  
10 scope of this invention involves not only the homopolymerization of the above-mentioned branched  $\alpha$ -olefins, but also the copolymerization of the above-mentioned branched  $\alpha$ -olefins and other olefins copolymerizable therewith. The "other olefins" usable for the copolymerization are  
15 straight or branched chain  $\alpha$ -olefins having 2 to 12 carbon atoms and straight chain internal olefins having 4 to 12 carbon atoms. Concrete examples <sup>hereof</sup> include ethylene, propylene, butene-1, pentene-1, hexene-1, octene-1, 4-methylpentene-1, 4-methylhexene-1, 5-methylhexene-1,  
20 butene-2, pentene-2 and hexene-2.

The polymerization is carried out in the presence of an inert hydrocarbon such as hexane, heptane or the like as a diluent. Alternatively, the polymerization is carried out in the state of a slurry by using the liquid  
25 monomer itself as a medium for the polymerization. The temperature of the polymerization is in the range of from 25° to 150°C. The polymerization is usually carried out under a pressure ranging from 1 atmosphere to about 50 atmospheres.

1 The mode of the polymerization may be any of/<sup>a</sup>continuous  
system and batch system. Further, various electron-  
donative compounds may also be added at the time of  
polymerization for the purpose of improving the activity  
5 of/<sup>the</sup>catalyst and/<sup>the</sup>stereospecificity. It is also allowable  
to add a chain transfer agent, such as hydrogen or the  
like for the purpose of regulating the molecular weight  
of the polymer.

Next, the process of this invention will be  
10 illustrated with reference to the following examples, but  
the invention is not limited thereto.

#### Example 1

##### (A) Synthesis of Solid Product

After replacing, with argon, the inner atmosphere  
15 of a flask having a capacity of 500 ml and/<sup>being</sup>equipped with  
a stirrer and a dropping funnel, 90 ml of n-heptane and  
100.5 ml of tetra-n-butoxytitanium were charged into the  
flask. While maintaining the inner temperature of the  
flask at 35°C, a solution composed of 162 ml of n-heptane  
20 and 67.2 ml of ethylaluminum sesquichloride ~~was slowly~~  
added dropwise into the flask from the dropping funnel  
over a period of 2 hours. After dropping it, the inner  
temperature was elevated to 60°C and the content of the  
flask was stirred for one hour. The flask was allowed to  
25 stand at room temperature and the reaction mixture was  
separated into solid and liquid phases, after which the  
solid product was washed four times with 100 ml of n-heptane



1 and dried under reduced pressure to obtain a red-brown  
colored solid product. One gram of this solid product  
contained 4.68 millimoles of titanium, 6.29 millimoles of  
n-butoxy group and 0.23 millimole of aluminum, and the  
5 ratio of n-butoxy group/titanium was 1.34 (by mole). In  
the X-ray diffraction spectrum of this solid product  
measured with Cu-K $\alpha$  rays, the characteristic peaks of  
titanium trichloride crystal were not found at all.

(B) Synthesis of <sup>the</sup> Solid Catalyst Component

10 After replacing the inner atmosphere of a flask  
having a capacity of 100 ml with argon, 6.95 g of the  
solid product prepared in (A) above and 35 ml of n-heptane  
were charged into the flask. While maintaining the inner  
temperature of the flask at 75°C, 5.2 ml of di-n-butyl  
15 ether and 6.8 ml of titanium tetrachloride were added and  
reacted at this temperature for 1 hour. The flask was  
allowed to stand at room temperature and the reaction  
mixture was separated into solid and liquid phases, after  
which the solid product was washed four times with 50 ml of  
20 n-heptane and then dried under reduced pressure to obtain  
~~a red-violet colored solid catalyst component.~~ One gram  
of this solid catalyst component contained 5.91 millimoles  
of titanium, 0.42 millimole of n-butoxy group and 0.01  
millimole of aluminum, and the ratio n-butoxy group/  
25 titanium was 0.071 (by mole). The X-ray diffraction  
spectrum of this solid catalyst component had diffraction  
lines corresponding to the diffraction lines of planes [113]  
and [300] of <sup>the</sup>  $\delta$ -form titanium trichloride.

1 (C) Polymerization of Vinylcyclohexane

After replacing, with argon, the inner atmosphere  
of a flask having a capacity of 100 ml and/equipped with  
a magnetic stirrer, 9.6 ml of n-heptane, 2.6 millimoles  
5 of triethylaluminum, 98.4 mg of the solid catalyst component  
obtained in (B) above and 5 ml of vinylcyclohexane were  
added. The inner temperature of the flask was elevated to  
50°C, and polymerization was carried out at this temper-  
ature for one hour. For the sake of after-treatment, the  
10 product was washed several times with 40 ml of a 1:9 (by  
volume) mixture of hydrochloric acid (hydrogen chloride  
content 36%) and methanol and then it was thoroughly washed  
with water. Then, it was washed twice with 40 ml of  
methanol, filtered and dried under reduced pressure to  
15 obtain a granular polymer. Yield of the granular polymer  
was 2.87 g. This means that the yield (g) of polyvinyl-  
cyclohexane per 1 g of solid catalyst component (herein-  
after, simply referred to as "Polym/Cat") was 29.2.

Comparative Example 1

20 Vinylcyclohexane was polymerized by repeating  
the procedure of Example 1-(C), except that the solid  
catalyst component obtained in Example 1-(B) was replaced  
with 101.5 mg of a commercially available titanium tri-  
chloride [this titanium trichloride had been prepared by  
25 reducing  $\text{TiCl}_4$  with organo-aluminum to obtain a complex  
compound of  $\text{TiCl}_3$  and  $\text{AlCl}_3$  (molar ratio Ca. 3:1), treating  
the complex with di-isoamyl ether to extract off the major

- 1 part of  $\text{AlCl}_3$  and then activating the residue by a  
treatment with  $\text{TiCl}_4$ ; 1 g of this solid catalyst component  
contained 6.05 millimoles of titanium and 0.16 millimole  
of aluminum]. / yield of /granular polymer was 0.51 g, and  
5 Polym/Cat was 5.0.

#### Example 2

- Vinylcyclohexane was polymerized by repeating  
the procedure of Example 1-(C), except that the solid  
catalyst component obtained in Example 1-(B) was used in  
10 an amount of 90.2 mg and the triethylaluminum was replaced  
with 2.6 millimoles of trimethylaluminum. / yield of /granular  
polymer was 1.65 g, and Polym/Cat was 18.3.

#### Example 3

- Vinylcyclohexane was polymerized by repeating  
15 the procedure of Example 1-(C), except that the solid  
catalyst component obtained in Example 1-(B) was used in  
an amount of 106.3 mg, the 2.6 millimoles of triethyl-  
aluminum was replaced with a mixture consisting of 1.3  
millimoles of triethylaluminum and 1.3 millimoles of  
20 diethylaluminum ethoxide and the time of the polymerization  
was 25 minutes. / yield of /granular polymer was 2.97 g,  
and Polym/Cat was 27.9.

#### Example 4

- A violet-colored solid catalyst component was  
25 prepared by repeating the procedure of Example 1-(B),

1 except that the reaction was carried out at 95°C for 2  
hours by using 9.69 g of the solid product obtained in  
Example 1-(A), 48.5 ml of n-heptane, 7.3 ml of di-n-butyl  
ether and 23.6 ml of titanium tetrachloride. One gram  
5 of this solid catalyst component contained 6.05 millimoles  
of titanium, 0.15 millimole of n-butoxy group and 0.01  
millimole of aluminum, and its n-butoxy group/titanium  
ratio was 0.025 (by mole). The X-ray diffraction spectrum  
of this solid catalyst component had diffraction lines  
10 corresponding to the diffraction lines of planes [113] and  
[300] of <sup>the</sup>δ-form titanium trichloride.

Then, vinylcyclohexane was polymerized by  
repeating the procedure of Example 1-(C), except that  
this solid catalyst component was used in an amount of  
15 87.9 mg. <sup>The</sup>Yield of <sup>the</sup>granular polymer was 1.15 g, and  
Polym/Cat was 13.1.

#### Example 5

A solid catalyst component was prepared by  
repeating the procedure of Example 1-(B), except that the  
20 reaction was carried out at 70°C for one hour by using  
11.41 g of the solid product obtained in Example 1-(A),  
57.1 mg of n-heptane, 8.5 ml of di-n-butyl ether and 8.3 ml  
of titanium tetrachloride. One gram of this solid  
catalyst component contained 5.41 millimoles of titanium,  
25 1.18 millimoles of n-butoxy group and 0.02 millimole of  
aluminum, and its n-butoxy group/titanium ratio was 0.218  
(by mole). The X-ray diffraction spectrum of this solid

- 1 catalyst component had diffraction lines corresponding  
to the diffraction lines of planes [113] and [300] of  
δ-form titanium trichloride. Then, vinylcyclohexane was  
polymerized by repeating the procedure of Example 1-(C),  
5 except that 94.7 mg of this solid catalyst component was  
used. <sup>The</sup> / <sup>the</sup> yield of/ granular polymer was 1.16 g, and Polym/Cat  
was 12.2.

#### Comparative Example 2

- A solid catalyst component was prepared by  
10 repeating the procedure of Example 1-(B), except that the  
reaction was carried out at 100°C for one hour by using  
4.42 g of the solid product obtained in Example 1-(A) and  
20 ml of titanium tetrachloride and using neither n-heptane  
nor di-n-butyl ether. One gram of this solid catalyst  
15 component contained 5.85 millimoles of titanium, 0.22  
millimole of n-butoxy group and 0.18 millimole of aluminum,  
and its n-butoxy group/titanium ratio was 0.038 (by mole).  
The X-ray diffraction spectrum of this solid catalyst  
component had the same diffraction lines as those of β-form  
20 titanium trichloride having a fibriform structure.

- Then, vinylcyclohexane was polymerized by  
repeating the procedure of Example 1-(C), except that  
107.4 mg of this solid catalyst component was used. <sup>The</sup> / yield  
of the granular polymer was 0.44 g, and Polym/Cat was  
25 4.1.

1 Comparative Example 3

A solid catalyst component was prepared by repeating the procedure of Example 1-(B), except that the reaction was carried out at 90°C for one hour by using  
5 6.62 g of the solid product obtained in Example 1-(A), 33.1 ml of n-heptane and 9.7 ml of titanium tetrachloride and using no di-n-butyl ether. One gram of this solid catalyst component contained 5.36 millimoles of titanium, 2.11 millimoles of n-butoxy group and 0.17 millimole of  
10 aluminum, and its n-butoxy group/titanium ratio was 0.394 (by mole). In the X-ray diffraction spectrum of this solid catalyst component, the characteristic peaks of titanium trichloride crystal were not found at all. Then, vinylcyclohexane was polymerized by repeating the procedure of  
15 Example 1-(C), except that 98.0 mg of this solid catalyst component was used. As the result, no granular polymer was formed at all.

Comparative Example 4

Vinylcyclohexane was polymerized by repeating  
20 the procedure of Example 1-(C), except that the solid product obtained in Example 1-(A) was used in an amount of 81.2 mg. As the result, no granular polymer was formed at all.

Example 6

the  
(A) Synthesis of/Solid Product

25 After replacing, with argon, the inner atmosphere

1 of a flask having a capacity of 500 ml and <sup>being</sup>/equipped with  
a stirrer and a dropping funnel, 100 g of tetra-o-cresoxy-  
titanium and 250 ml of toluene were charged into the flask  
and the tetra-o-cresoxytitanium was dissolved. Then,  
5 while maintaining the inner temperature of the flask at  
60°C, a solution composed of 100 ml of toluene and 47.8 ml  
of ethylaluminum sesquichloride was slowly added dropwise  
thereinto from the dropping funnel over a period of 2  
hours. After dropping it, the content of the flask was  
10 stirred at 60°C for one hour. Then, the flask was allowed  
to stand at room temperature and the reaction mixture was  
separated into solid and liquid phases, after which the  
solid product was washed four times with 200 ml of n-  
heptane and dried under reduced pressure to obtain a brown-  
15 colored solid product. One gram of this solid product  
contained 3.8 millimoles of titanium and 4.7 millimoles of  
o-cresoxy group. In the X-ray diffraction spectrum of  
this solid product measured with Cu-K $\alpha$  rays, no characteris-  
tic peaks of titanium trichloride crystal were found at all.  
20 (B) Synthesis of <sup>the</sup>Solid Catalyst Component .

After replacing the inner atmosphere of a flask  
having a capacity of 100 ml with argon, 6.3 g of the  
solid product synthesized in (A) above and 32 ml of n-  
heptane were charged into the flask and the inner temper-  
25 ature of the flask was maintained at 30°C. Then, 5.7 ml  
of di-isoamyl ether was added and treated at 35°C for  
one hour. Subsequently, 6.2 ml of titanium tetrachloride  
was added, the temperature was elevated to 65°C, and

1 the content of the flask was reacted at 65°C for one hour.  
The flask was allowed to stand at room temperature and the  
reaction mixture was separated into solid and liquid  
phases, after which the solid product was washed five  
5 times with 50 ml of n-heptane and dried under reduced  
pressure to obtain a solid catalyst component.

One gram of this solid catalyst component contained  
5.3 millimoles of titanium, 0.19 millimole of o-cresoxy  
group and 0.02 millimole of aluminum, and its o-cresoxy  
10 group/titanium ratio was 0.036 (by mole). The X-ray dif-  
fraction spectrum of this solid catalyst component had  
diffraction lines corresponding to the diffraction lines  
of planes [113] and [300] of <sup>the</sup>δ-form titanium trichloride.

(C) Polymerization of Vinylcyclohexane

15 Vinylcyclohexane was polymerized by repeating  
the procedure of Example 1-(C), except that 75.4 mg of  
the solid catalyst component obtained in (B) above was used.  
As the result, <sup>the</sup> yield of <sup>the</sup> granular polymer was 1.83 g, and  
Polym/Cat was 24.3.

20 Example 7

(A) Synthesis of <sup>the</sup> Solid Product

After replacing, with argon, the inner atmosphere  
of a flask having a capacity of 300 ml and <sup>being</sup> equipped with  
a stirrer and a dropping funnel, 15 ml of n-heptane and  
25 15 ml of titanium tetrachloride were charged into the  
flask, and the inner temperature of the flask was maintained  
at 80°C. Then, while maintaining the inner temperature of



1 the flask at 80°C, a solution composed of 40 ml of n-heptane  
and 52 ml of n-decyl alcohol was slowly added dropwise  
thereinto from the dropping funnel over a period of one  
hour. After dropping it, the content of the flask was  
5 stirred at 80°C for 1.5 hours. After lowering the inner  
temperature of the flask to 50°C, a solution composed of  
40 ml of n-heptane and 17 ml of diethylaluminum chloride  
was slowly added dropwise thereinto from the dropping  
funnel over a period of 2 hours, while maintaining the  
10 inner temperature of the flask at 50°C. After dropping it,  
the temperature was elevated to 60°C, and the content of  
the flask was stirred for one hour. The flask was allowed  
to stand at room temperature and the reaction mixture  
was separated into solid and liquid phases, after which  
15 the solid product was washed six times with 100 ml of  
n-heptane and dried under reduced pressure to obtain a  
brown-colored solid product.

(B) Synthesis of <sup>the</sup>/Solid Catalyst Component

A solid catalyst component was prepared by  
20 repeating the procedure of Example 1-(B), except that  
6.75 g of the solid product obtained in (A) above, 24 ml of  
n-heptane, 10 ml of monochlorobenzene, 4.1 ml of di-n-butyl  
ether and 5.4 ml of titanium tetrachloride were used. One  
gram of this solid catalyst component contained 5.1 milli-  
25 moles of titanium, 0.17 millimole of n-decylalkoxy group  
and 0.02 millimole of aluminum, and the n-decylalkoxy  
group/titanium ratio was 0.033 (by mole). The X-ray dif-  
fraction spectrum of this solid catalyst component had

- 1 diffraction lines corresponding to the diffraction lines  
of planes [113] and [300] of <sup>the</sup>  $\delta$ -form titanium trichloride.

(C) Polymerization of Vinylcyclohexane

- Vinylcyclohexane was polymerized by repeating  
5 the procedure of Example 1-(C), except that 131.1 mg  
of the solid catalyst component obtained in (B) above was  
used and the time of the polymerization was 25 minutes. The  
yield of <sup>the</sup> granular polymer was 1.94 g, and Polym/Cat was  
14.8.

10 Example 8

(A) Synthesis of <sup>the</sup> Heat-treated Solid Product

- After replacing, with argon, the inner atmosphere  
of a four-necked flask having a capacity of 500 ml and  
equipped with a stirrer and a dropping funnel, 114 ml  
15 of n-heptane and 30 ml of titanium tetrachloride were  
charged into the flask and <sup>the</sup> temperature of the resulting  
solution was maintained at  $-10^{\circ}\text{C}$ . Then, while maintaining  
the inner temperature of the flask at  $-5^{\circ}\text{C}$  to  $-10^{\circ}\text{C}$ , a  
solution composed of 150 ml of n-heptane and 68.3 ml of  
20 ethylaluminum sesquichloride was added dropwise thereinto  
from the dropping funnel over a period of 2 hours. After  
dropping it, the content of the flask was stirred at  
room temperature for 30 minutes. Then, the temperature  
was elevated to  $65^{\circ}\text{C}$ , and a heat-treatment was carried at  
25 this temperature for 2 hours. Then, the flask was allowed  
to stand at room temperature and the reaction mixture  
was separated into solid and liquid phases, after which

1 the solid product was washed four times with 200 ml of  
n-heptane and dried under reduced pressure to obtain a  
heat-treated solid product.

(B) Synthesis of/<sup>the</sup>Solid Catalyst Component

5 After replacing, with argon, the inner atmosphere  
of a flask having a capacity of 200 ml and/<sup>being</sup>equipped with  
a stirrer, 91.5 ml of n-heptane, 24.0 ml of di-isoamyl  
ether and 3.0 g of iodine were charged into the flask, and  
the iodine was dissolved at 50°C for 30 minutes. Then,  
10 18.3 g of the heat-treated solid product obtained in (A)  
above was charged into the flask and reacted at 95°C for  
one hour. After the reaction, the reaction mixture was  
cooled to 65°C, 30 ml of a titanium compound represented  
by  $\text{Ti}(\text{OBu})_{0.5}\text{Cl}_{3.5}$  was added, and the reaction mixture  
15 was treated at 65°C for 30 minutes. Then, the flask was  
allowed to stand at room temperature and the reaction  
mixture was separated into solid and liquid phases, after  
which the solid product was washed five times with 50 ml  
of n-heptane and dried under reduced pressure to obtain  
20 a violet-colored solid catalyst component. One gram of  
this solid catalyst component contained 5.8 millimoles of  
titanium, 0.21 millimole of n-butoxy group and 0.41 milli-  
mole of aluminum, and its n-butoxy group/titanium ratio  
was 0.036 (by mole). The X-ray diffraction spectrum of  
25 this solid catalyst component had diffraction lines cor-  
responding to the diffraction lines of planes [003], [113]  
and [300] of/<sup>the</sup> $\delta$ -form titanium trichloride.

## 1 (C) Polymerization of Vinylcyclohexane

Vinylcyclohexane was polymerized by repeating the procedure of Example 1-(C), except that 95.8 mg of the solid catalyst component obtained in (B) above was used.

5 As the result, <sup>the</sup>yield of <sup>the</sup>granular polymer was 2.53 g, and Polym/Cat was 26.4.

WHAT IS CLAIMED IS:

1. A process for homopolymerizing an  $\alpha$ -olefin branched at the carbon atom of the third position or copolymerizing said  $\alpha$ -olefin with another olefin in the presence of a catalyst system comprising a combination of an organo-aluminum compound and a solid catalyst component containing titanium, chlorine and <sup>a</sup>hydrocarbyloxy group, of which <sup>the</sup> x-ray diffraction spectrum has diffraction lines at least corresponding to the diffraction lines of planes [113] and [300] of titanium trichloride having a layer structure and wherein the content of the hydrocarbyloxy group is 0.01 mole to 0.3 mole per 1 mole of titanium.

2. A process according to Claim 1, wherein said hydrocarbyloxy group is represented by the following general formula:



wherein  $\text{R}^1$  represents <sup>a</sup>hydrocarbon group having 1 to 20 carbon atoms.

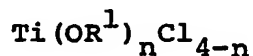
3. A process according to Claim 2, wherein  $\text{R}^1$  in the general formula  $\text{OR}^1$  is a straight chain alkyl group having 2 to 18 carbon atoms or an aryl group having 6 to 18 carbon atoms.

4. A process according to Claim 1, wherein the content of the hydrocarbyloxy group is 0.02 mole to 0.25 mole per 1 mole of titanium.

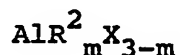
5. A process according to Claim 1, wherein the

X-ray diffraction spectrum of said solid catalyst component has diffraction lines at least corresponding to the diffraction lines of planes [113] and [300] of <sup>the</sup>  $\delta$ -form titanium trichloride.

6. A process according to Claim 1, wherein said solid catalyst component is a solid catalyst component synthesized by reducing a titanium compound represented by the following general formula:



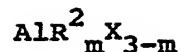
wherein  $\text{R}^1$  represents <sup>a</sup>hydrocarbon group having 1 to 20 carbon atoms and  $n$  represents a numerical figure satisfying  $0 < n \leq 4$ , with an organo-aluminum compound represented by the following general formula:



wherein  $\text{R}^2$  represents <sup>a</sup>hydrocarbon group having 1 to 20 carbon atoms,  $\text{X}$  represents <sup>a</sup>halogen atom and  $m$  represents a numerical figure satisfying  $1 < m \leq 3$ , to obtain a hydrocarbyloxy group-containing solid product insoluble in hydrocarbon solvents, followed by treating said solid product at a temperature of 45°C to 120°C in the presence of an ether compound and titanium tetrachloride in the state of a slurry.

7. A process according to Claim 1, wherein said solid catalyst component is a solid catalyst component synthesized by reducing titanium tetrachloride with an organo-aluminum compound represented by the following

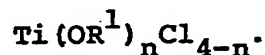
general formula:



wherein  $\text{R}^2$ , X and m are each as defined above, followed by heat-treating the reduced product at a temperature not higher than 150°C, reacting the heat-treated product with a mixture consisting of a halogen compound represented by the following general formula:



wherein X represents <sup>a</sup>/halogen atom, and an ether compound in a hydrocarbon solvent, and then treating the reaction product with a titanium compound represented by the following general formula:



wherein  $\text{R}^1$  and n are each as defined above.

8. A process according to Claim 1, wherein the organo-aluminum compound used for the polymerization is trialkylaluminum, dialkylaluminum hydride, dialkylaluminum chloride, dialkylaluminum alkoxide, dialkylaluminum siloxide or a mixture thereof.

9. A process according to Claim 8, wherein the organo-aluminum compound is trimethylaluminum, triethylaluminum, triisobutylaluminum, diethylaluminum ethoxide or a mixture thereof.

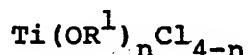
10. A process according to Claim 1, wherein the organo-aluminum compound used for the polymerization is used in

an amount ranging from 0.5 mole to 100 moles per 1 mole of titanium atom present in the solid catalyst component.

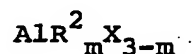
11. A process according to Claim 1, wherein said  $\alpha$ -olefin branched at the carbon atom of the third position is 3-methylbutene-1 or vinylcyclohexane.

12. A process according to Claim 1, wherein the temperature of the polymerization is in the range of from 25° to 150°C.

13. A solid catalyst component synthesized by reducing a titanium compound represented by the following general formula:



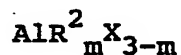
wherein  $\text{R}^1$  represents a hydrocarbon group having 1 to 20 carbon atoms and  $n$  represents a numerical figure satisfying  $0 < n \leq 4$ , with an organo-aluminum compound represented by the following general formula:



wherein  $\text{R}^2$  represents a hydrocarbon group having 1 to 20 carbon atoms,  $\text{X}$  represents a halogen atom and  $m$  represents a numerical figure satisfying  $1 < m \leq 3$ , to obtain a hydrocarbyloxy group-containing solid product insoluble in hydrocarbon solvents, followed by treating said solid product at a temperature of 45°C to 120°C in the presence of an ether compound and titanium tetrachloride in the state of a slurry.



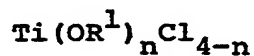
14. A solid catalyst component synthesized by reducing titanium tetrachloride with an organo-aluminum compound represented by the following general formula:



wherein  $\text{R}^2$ , X and m are each as defined above, followed by heat-treating the reduced product at a temperature not higher than  $150^\circ\text{C}$ , reacting the heat-treated product with a mixture comprising a halogen compound represented by the general formula:



wherein X represents a halogen atom, and an ether compound in a hydrocarbon solvent, and then treating the reaction product with a titanium compound represented by the following general formula:



wherein  $\text{R}^1$  and n are each as defined above.